

GALLIUM AND INDIUM  
ANNUAL SURVEY COVERING THE YEAR 1979

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Introduction, Reviews, and Books

This survey describes topics on organogallium and -indium reported during 1979 in the order of 'Reviews and Books', 'Structure and Bonding (including synthesis)', and 'Synthesis, Analysis, and Reaction Chemistry' including one patent.

A review on 'Group III Elements: Aluminium, Gallium, Indium, and Thallium' with an extensive bibliography [1], and a book containing a chapter on 'Organic Compounds of Group III Metals' with 149 references [2] have been published.

Structure and Bonding (including Synthesis)

Although phenylgallium halides,  $(C_6H_5)_nGaX_{3-n}$  ( $X = Cl, Br; n = 1, 2$ ), are known to be dimeric in benzene, no solid state structure has been reported so far. The IR, Raman, mass, and, where possible,  $^{69,71}Ga$  nuclear quadrupole resonance (NQR) spectra of the complete series of  $(C_6H_5)_nGaX_{3-n}$  ( $X = Cl, Br, I; n = 1, 2$ ) have been studied [3]. The results indicated the existence of discrete halogen-bridged molecular dimers for each compound in the solid state, which are similar to the arylaluminium halides. Only  $C_6H_5GaCl_2$  produced a NQR spectrum, which suggests the presence of two crystallographically inequivalent Ga atoms in the solid state.

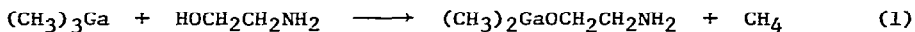
The reactions of  $(CH_3)_3Ga$  with  $ClN_3$  (in benzene),  $NH_3$  (in diethyl ether) or  $Na^{15}N_3$  (in benzene) were reported to give dimethylgallium azide trimer,  $[(CH_3)_2GaN_3]_3$ . Variable temperature  $^{15}N$ -NMR spectra of the  $^{15}N$  enriched azide in the  $-90$  to  $+35^\circ C$  range have demonstrated that rapid exchange of the azido groups occurs at room temperature on the NMR time scale. The IR and Raman spectra of

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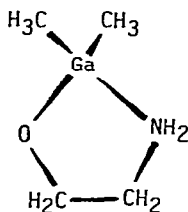
Gallium and Indium; Annual Survey covering the year 1978 see *J. Organometal. Chem.*, 180 (1979) 101-109.

$[(\text{CH}_3)_2\text{Ga}^{14}\text{N}_3]_3$  and  $[(\text{CH}_3)_2\text{Ga}^{15}\text{N}_3]_3$  also have been assigned [4].

Trimethylgallium also reacts with ethanolamine in refluxing benzene to yield 2-aminoethoxydimethylgallium (Eq. 1), which is an extremely air- and

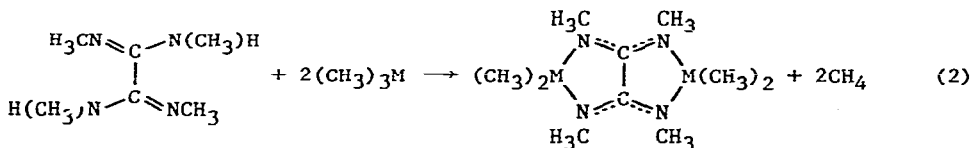


moisture-sensitive white solid. Infrared,  $^1\text{H-NMR}$ , and mass spectra of this compound were examined. An X-ray diffraction study has revealed that the solid consists of monomeric molecules in which the Ga atoms are in a distorted tetrahedral environments (1). The molecules are linked by an extensive network of



1

$\text{N-H}\cdots\text{O}$  hydrogen bonds [5]. This structure is quite different from that of the  $\text{N,N}$ -dimethyl derivatives,  $\text{R}_2\text{GaOCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$  ( $\text{R} = \text{H}, \text{CH}_3$ ), which consists of well-separated dimeric units containing five-coordinate Ga atoms (S. J. Rettig, A. Storr, and J. Trotter, *Can. J. Chem.*, 53 (1975) 58). The reaction of  $\text{N,N}',\text{N}'',\text{N}'''$ -tetramethyloxamidine with the trimethyl derivatives of Al, Ga, and In at 1:2 mole ratio afforded monomeric bis(dimethylmetal)oxamidines (2 in Eq. 2). The X-ray structure determination as well as the IR and Raman spectra



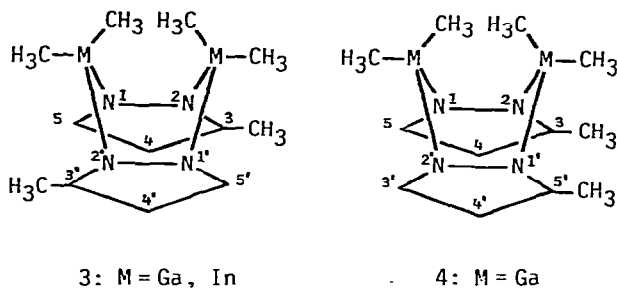
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$\text{M} = \text{Al}, \text{Ga}, \text{In}$

confirmed that the molecules consist of two fused five-membered rings with an essentially planar structure [6].

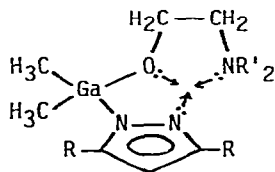
There is considerable interest in the coordination properties of pyrazolyl derivatives of the Group III elements. Thus, dimeric 3-methylpyrazolyl (mepz) and indazolyl (ind) dimethyl derivatives of Ga and In,  $[(\text{CH}_3)_2\text{M}(\text{mepz})]_2$  and  $[(\text{CH}_3)_2\text{M}(\text{ind})]_2$  ( $\text{M} = \text{Ga}, \text{In}$ ), were prepared by the reaction of 3-methylpyrazole

or indazole with the appropriate trimethylmetal compound [7]. The  $^1\text{H-NMR}$  spectra have indicated that  $[(\text{CH}_3)_2\text{Ga}(\text{mepz})]_2$  exists as an isomeric pair of 3 and 4, both of which assume boat configurations, in the approximate ratio of 9:1. On the other hand,  $[(\text{CH}_3)_2\text{In}(\text{mepz})]_2$  gives a single species, 3. The



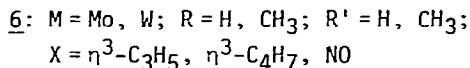
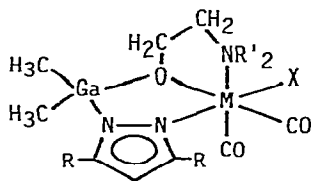
indazolyl derivatives of Ga and In also exist as a single structural isomer, in which the twelve (M)-CH<sub>3</sub> protons are equivalent. An independent X-ray diffraction study had shown a boat configuration for  $[(\text{CH}_3)_2\text{Ga}(\text{ind})]_2$  (D. F. Rendle, A. Storr, and J. Trotter, *Can. J. Chem.*, 53 (1975) 2930).

Asymmetric tridentate gallate ligands incorporating pyrazolyl and 2-aminoethoxy substituents (5) have been the subject to recent publications. Thus,



5: R = H, CH<sub>3</sub>; R' = H, CH<sub>3</sub>

the reactions of sodium salts of these anions with  $\text{Mo}(\text{CO})_6$ ,  $\text{W}(\text{CO})_6$ , and  $\text{Mn}(\text{CO})_5^-$  Br in tetrahydrofuran were performed to give complexes of type  $\text{Na}^+[\text{LM}(\text{CO})_3]^-$  (M = Mo, W, Mn; L = anionic ligands 5). The Mo and W complexes reacted further with an excess of an appropriate allyl halide or with isoamyl nitrite in the same solvent, affording a variety of the mixed allyl-carbonyl or nitrosyl-carbonyl compounds (6). Analyses of their mass, IR, and  $^1\text{H-NMR}$  spectra have suggested that all the complexes are monomeric, octahedral species in *facial* coordination [8]. The tridentate chelate character of the gallate ligand and the *facial* nature of its coordination have unequivocally been confirmed by the X-ray structure analysis of  $[(\text{CH}_3)_2\text{Ga}(\text{N}_2\text{C}_5\text{H}_7)(\text{OCH}_2\text{CH}_2\text{NH}_2)]\text{Mo}(\text{CO})_2(\eta^3\text{-C}_4\text{H}_7)$  [9].



The Mo atom is in a distorted octahedral environment with the  $\eta^3$ -C<sub>4</sub>H<sub>7</sub> ligand occupying one of the six coordination sites, and the Ga atom is tetrahedrally coordinated to two CH<sub>3</sub> groups, a 2-aminoethoxy oxygen atom, and a pyrazolyl nitrogen atom.

Iodonickel nitrosyl reacts with the methyltris(pyrazolyl)gallate anion, [CH<sub>3</sub>Ga(N<sub>2</sub>C<sub>3</sub>H<sub>3</sub>)<sub>3</sub>]<sup>-</sup>, and its 3,5-dimethylpyrazolyl derivative, [CH<sub>3</sub>Ga(N<sub>2</sub>C<sub>5</sub>H<sub>7</sub>)<sub>3</sub>]<sup>-</sup>, as well as the anion  $\underline{5}$  to give four-coordinate nickel nitrosyl complexes of type LNi(NO) (L = the pyrazolyl gallate ligands). The X-ray structure analysis of the Ni complex of  $\underline{5}$  with R, R' = CH<sub>3</sub> has demonstrated that the Ni atom is in a severely distorted tetrahedral environment (Fig. 1), whereas the variable

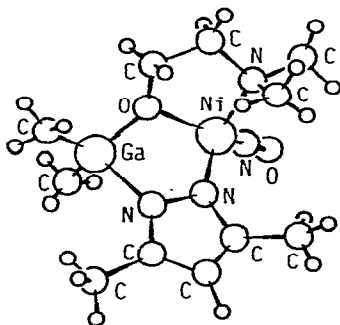


Fig. 1. Molecular structure of [(CH<sub>3</sub>)<sub>2</sub>Ga(N<sub>2</sub>C<sub>5</sub>H<sub>7</sub>)-(OCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>)]Ni(NO)

temperature <sup>1</sup>H-NMR spectra have indicated a stereochemical non-rigidity for the complex in toluene-*d*<sub>8</sub> at room temperature [10]. The anionic ligand  $\underline{5}$  with R, R' = CH<sub>3</sub> reacts also with Fe(NO)<sub>2</sub>I in tetrahydrofuran to afford the formally 19-electron iron nitrosyl complex, [(CH<sub>3</sub>)<sub>2</sub>Ga(N<sub>2</sub>C<sub>5</sub>H<sub>7</sub>)(OCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>)]Fe(NO)<sub>2</sub>. The analogous Mn dinitrosyl complex also was obtained from  $\underline{5}$  (R, R' = CH<sub>3</sub>), [(CH<sub>3</sub>O)<sub>3</sub>P]<sub>2</sub>Mn(NO)<sub>2</sub>Br, and AgPF<sub>6</sub> [11]. The structure of the Fe complex was determined by an X-ray analysis; the crystal structure consists of discrete monomeric units. The coordination geometry around the Fe atom is that of a

distorted trigonal bipyramid, with the tridentate gallate ligand acting in a *meridional* fashion, occupying one equatorial and two axial positions. The  $^1\text{H-NMR}$  spectrum of the Mn complex is satisfactorily explained by assuming a trigonal bipyramidal configuration with equatorial NO groups and a *meridional* gallate ligand, similar to the solid state structure of the Fe complex.

The reaction of  $(\text{CH}_3)_3\text{Ga}$  with  $\text{CH}_3\text{NH}_2$  in toluene in a sealed ampoule at  $210^\circ\text{C}$  for 15 h gave the product formulated as  $[(\text{CH}_3)_2\text{GaNH}(\text{CH}_3)]_2[\text{CH}_3\text{GaNCH}_3]_6$  [12]. The cage structure of this compound (Fig. 2) has been shown by an X-ray crystallographic analysis. The  $(\text{CH}_3)_2\text{GaNH}(\text{CH}_3)$  fragments are disordered and

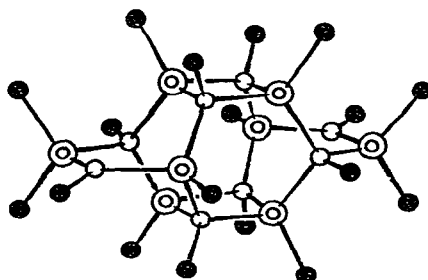
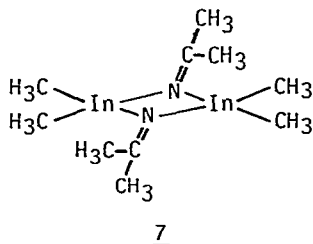


Fig. 2. Molecular structure of  $[(\text{CH}_3)_2\text{GaNH}(\text{CH}_3)]_2[\text{CH}_3\text{GaNCH}_3]_6$ ,  
 ⊙: Ga, ○: N, ●: C.

there are two isomers, *cis* and *trans*, in which two  $(\text{CH}_3)_2\text{GaNH}(\text{CH}_3)$  groups are related by a  $C_2$  and a  $C_1$  axis. The *cis* and *trans* isomers have been detected also in the  $^1\text{H-NMR}$  spectrum in hydrocarbon solution.

Müller et al. have reported the reaction of  $(\text{CH}_3)_3\text{In}$  with N-chloro-2-propanimine,  $(\text{CH}_3)_2\text{C}=\text{NCl}$ , in cyclohexane at  $40^\circ\text{C}$ , which yielded (isopropylidene-amino)dimethylindium dimer,  $[(\text{CH}_3)_2\text{InN}=\text{C}(\text{CH}_3)_2]_2$ . The centrosymmetric molecular structure with a four-membered  $(\text{InN})_2$  ring (7) has been deduced from vibrational,



$^1\text{H-NMR}$ , and mass spectra, and confirmed by an X-ray structure determination. There are two dimeric molecules per unit cell with  $a = 856(1)$ ,  $b = 1399(1)$ ,  $c = 733(1)$  pm, and  $\beta = 106.6(0.1)^\circ$  in the space group  $P2_1/c$  [13].

### Synthesis, Analysis, and Reaction Chemistry

The low temperature deposition of metal vapors with a large excess of solvents, followed by warming and subsequent partial reclustering (bond formation) of metal atoms, allows preparation of very active metal particles in slurry form. Thus, slurries of Al and In as well as of a variety of other metals were obtained in organic solvents [14]. These metal-organic dispersions were allowed to react with alkyl and aryl halides;  $(\text{In})_n/\text{solvent}$  with  $\text{C}_2\text{H}_5\text{I}$  yielded mixtures of  $(\text{C}_2\text{H}_5)_2\text{InI}$ ,  $\text{C}_2\text{H}_5\text{InI}_2$ , and  $\text{InI}$ . The yields were highest when high boiling, polar solvents such as diglyme and dioxane were employed. The active powders prepared from the slurries by solvent evaporation are storable for many months without significant loss in activity.

A patent reported that  $(\text{CH}_3)_3\text{Ga}$  was obtained by the reaction of  $(\text{CH}_3)_2\text{AlX}$  ( $\text{X} = \text{halide}$ ) with  $\text{RR}^1\text{R}^2\text{Ga}$  ( $\text{R} = \geq \text{C}_2$  hydrocarbon residues;  $\text{R}^1, \text{R}^2 = \text{H}$  or  $\geq \text{C}_2$  hydrocarbon residues) [15]. Thus, a mixture of 279 g  $(\text{C}_2\text{H}_5)_3\text{Ga}$  and 438 g  $(\text{CH}_3)_2\text{AlCl}$  in xylene was kept at  $100^\circ\text{C}$  for 2 h under dry nitrogen to give 263 g  $(\text{CH}_3)_3\text{Ga}$ . The latter is useful as a catalyst for olefin polymerization and a starting material for semi-conductive substances.

Surface-bound products produced at the gas-solid interface by the reaction of silica surfaces with  $\text{BCl}_3$ ,  $\text{Al}_2\text{Cl}_6$ ,  $(\text{CH}_3)_6\text{Al}_2$ , and others have been observed by IR spectroscopy. A similar study was carried out with the reaction between silica surfaces and  $(\text{CH}_3)_3\text{Ga}$ , followed by treatment with  $\text{HCl}$  [16]. The resulting silica-bound- $\text{OGaCl}_2$  catalyzes the reaction of  $\text{HCl}$  with  $\text{SiH}_4$  at room temperature, giving  $\text{H}_2$  and  $\text{H}_3\text{SiCl}$ . Another catalyst, of much smaller surface area but similar activity, was formed by  $(\text{CH}_3)_3\text{Ga}$  and  $\text{HCl}$  treatments of a cleaned Pyrex reaction vessel.

Two synthetic routes may be general to the air- and moisture-sensitive trialkyl(aryl)gallium and -indium compounds; one is the Grignard method and the other the metal displacement reaction using mercurials. In the latter route, the starting materials are easy to handle and the products obtained are reasonably pure. Thus, a number of substituted triaryl-gallium and -indium compounds (Table 1) were prepared by the reaction of Ga or In powder with the appropriate diarylmercurials in a Schlenk flask at elevated temperatures under nitrogen. The electron impact mass spectra under carefully controlled conditions have provided evidence for dimers of these compounds as significant

Table 1. Triaryl-gallium and -indium compounds

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|                         |  |
|-------------------------|--|
| $\text{R}_3\text{Ga}$ : | $\text{R} = \text{C}_6\text{H}_5$ , 2-, 3-, and 4- $\text{CH}_3\text{C}_6\text{H}_4$ , 4- $\text{C}_2\text{H}_5\text{C}_6\text{H}_4$ , 4- <i>t</i> - $\text{C}_4\text{H}_9\text{C}_6\text{H}_4$ ,<br>4- $\text{CH}_3\text{OC}_6\text{H}_4$ , 3- and 4- $\text{FC}_6\text{H}_4$ , 2-, 3-, and 4- $\text{ClC}_6\text{H}_4$ ,<br>3- and 4- $\text{BrC}_6\text{H}_4$ |
| $\text{R}_3\text{In}$ : | $\text{R} = \text{C}_6\text{H}_5$ , 2-, 3-, and 4- $\text{CH}_3\text{C}_6\text{H}_4$ , 4- $\text{C}_2\text{H}_5\text{C}_6\text{H}_4$ , 4- <i>t</i> - $\text{C}_4\text{H}_9\text{C}_6\text{H}_4$ ,<br>4- $\text{CH}_3\text{OC}_6\text{H}_4$ , 3- and 4- $\text{FC}_6\text{H}_4$ , 4- $\text{ClC}_6\text{H}_4$   |

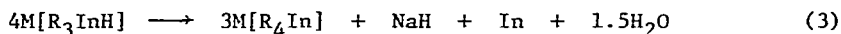
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species in the gaseous state [17]. A mass spectrometric study of alkyl derivatives of gallium was reported also by Postnikova et al. [18].

The reaction of  $\text{InCl}_3$  with the Grignard reagent  $(\text{CH}_3)_3\text{SiCH}_2\text{MgCl}$  in diethyl ether under argon has been studied [19]. This reaction gave tris(trimethylsilylmethyl)indium,  $[(\text{CH}_3)_3\text{SiCH}_2]_3\text{In}$ , in 80% yield. This product is a liquid at room temperature and exists as a monomeric, three-coordinate species. It undergoes an exchange reaction with  $\text{InCl}_3$  in benzene or diethyl ether, or cleavage by  $\text{HCl}$  in toluene on heating to afford the white crystalline chloro derivatives,  $[(\text{CH}_3)_3\text{SiCH}_2]_2\text{InCl}$  or  $(\text{CH}_3)_3\text{SiCH}_2\text{InCl}_2$ , depending on the mole ratio of the reactants, almost quantitatively. Molecular weight determinations of these chloro derivatives in benzene are consistent with chlorine-bridged dimeric structures.

Thermal decompositions of  $(\text{CH}_3)_3\text{In}$ ,  $(\text{CH}_3)_3\text{In}[\text{O}(\text{C}_2\text{H}_5)_2]$ , and  $(\text{C}_2\text{H}_5)_3\text{In}$  were examined in the 250–500°C range to afford In metal and gaseous product,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , etc., whose composition depended on the temperature. The decomposition reaction has been suggested to proceed *via* a free radical mechanism [20]. Solomatin et al. reported the determination of a variety of trace elements present as impurities in alkyl and alkoxy compounds of Group II–VI elements, including  $(\text{CH}_3)_3\text{Ga}[\text{O}(\text{C}_2\text{H}_5)_2]$  and  $(\text{C}_2\text{H}_5)_3\text{In}$ , by emission spectroscopy after conversion into oxides [21]. The detection limits were  $5 \times 10^{-3}\%$  for Zn in  $(\text{C}_2\text{H}_5)_3\text{In}$ .

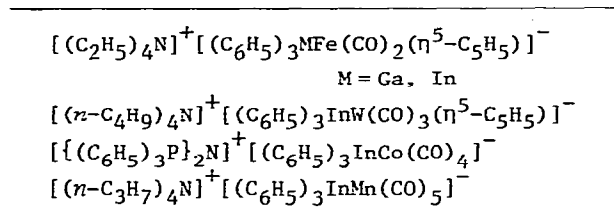
Trialkylindium reacts with alkali metal hydrides to yield metal salts of type  $\text{M}[\text{R}_3\text{InH}]$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ;  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ ), which can be converted to the tetraalkylindates on heating at 100°C, as shown in Eq. 3. The  $\text{Na}[(\text{C}_2\text{H}_5)_2\text{InH}_2]$  salt



also can be prepared by the reaction of  $(\text{C}_2\text{H}_5)_2\text{InCl}$  with  $\text{NaH}$  [22]. The interaction of  $(\text{CH}_3)_3\text{M}^{\text{III}}$  or  $(\text{CH}_3)_2\text{M}^{\text{III}}\text{X}$  with  $(\text{CH}_3)_3\text{M}^{\text{V}}\text{X}_2$  and  $(\text{CH}_3)_4\text{M}^{\text{V}}\text{X}$ , respectively, was reported to give methylhalogeno metalates of the general composition  $[(\text{CH}_3)_4\text{M}^{\text{V}}]^{+}[(\text{CH}_3)_{4-n}\text{M}^{\text{III}}\text{X}_n]^{-}$ , where  $\text{M}^{\text{V}} = \text{As}, \text{Sb}$ ;  $\text{M}^{\text{III}} = \text{Ga}, \text{In}$ ;  $\text{X} = \text{Br}, \text{I}$ ;  $n = 1-3$ . Infrared, Raman, and  $^1\text{H}$ -NMR spectra of these ionic compounds have been discussed in terms of their structures [23].

Numerous coordination complexes of triphenylmetal acceptors,  $(\text{C}_6\text{H}_5)_3\text{M}$  ( $\text{M} = \text{B}, \text{Al}, \text{Ga}, \text{In}$ ) with neutral main group Lewis bases have been reported, but relatively few anionic complexes are known. Thus, the reactions of  $(\text{C}_6\text{H}_5)_3\text{M}$  ( $\text{M} = \text{Al}, \text{Ga}, \text{or In}$ ) with metal carbonyl anions with the formula  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^{-}$ ,  $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3]^{-}$ ,  $[\text{Co}(\text{CO})_4]^{-}$ , and  $[\text{Mn}(\text{CO})_5]^{-}$  were carried out in dichloromethane or in tetrahydrofuran [24]. The crystalline Ga and In compounds isolated are listed in Table 2. The analysis of their IR spectra, especially in the  $\nu(\text{C}=\text{O})$  region, in mineral oil mulls has suggested the presence of a metal-metal bond in all the complexes. The presence of the metal-metal

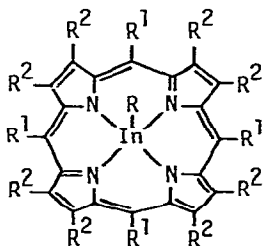
Table 2. Metal carbonyl anion complexes with triphenylgallium and -indium



bond has been confirmed by the single crystal X-ray study of the analogous Al-Fe complex,  $[(C_2H_5)_4N]^+[(C_6H_5)_3AlFe(CO)_2(\eta^5-C_5H_5)]^-$ . Although the Ga-W analog,  $[(n-C_4H_9)_4N]^+[(C_6H_5)_3GaW(CO)_3(\eta^5-C_5H_5)]^-$ , has not been isolated as a solid, the IR spectrum of an equimolar mixture of the donor and the acceptor in dichloromethane has suggested the coexistence of two isomeric compounds; one is a Ga-W bonded species and the other a species involving a Ga-O≡C-W link.

The reaction of dimethyl(methylperoxy)gallium,  $(CH_3)_2GaOOCH_3$ , with methanol in carbon tetrachloride, hexane, or anisole was reported to yield  $CH_3OOH$  and  $(CH_3)_2GaOCH_3$  [25]. This reaction is reversible and the equilibrium constant in carbon tetrachloride was determined. Other work on Group III metal peroxides resulted in a procedure for the quantitative analysis of hydrolyzed thermal decomposition products of  $(CH_3)_2GaOOCH_3$  and  $(CH_3)_2MOO-t-C_4H_9$  ( $M = Ga, In$ ) [26]. These dimethylmetal peroxides were dissolved in solvents and determined by reaction gas chromatography. By using a flame ionization detector and He as the carrier gas,  $CH_3OOH$ ,  $t-C_4H_9OOH$ ,  $CH_3OH$ ,  $t-C_4H_9OH$ , and  $(CH_3)_2CO$  were determined on a column filled with 30% dinonyl phthalate on celite 544. The standard deviation was 0.05 for the determination of 0.01-0.17 mole dimethylmetal peroxides/dm<sup>3</sup>.

A variety of new indium tetraphenylporphyrins (TPP) and octaethylporphyrins (OEP) containing an In-C bond (8) were synthesized by the reaction of (TPP)InCl or (OEP)InCl with alkyl- or aryllithium reagents. They were fully characterized by spectroscopic (mass, <sup>1</sup>H-NMR, IR, visible, and UV) measurements [27].



- 8:  $R^1 = C_6H_5$  and  $R^2 = H$  (TPP);  
 $R^1 = H$  and  $R^2 = C_2H_5$  (OEP);  
 $R = CH_3, C_2H_5, i-C_3H_7,$   
 $n-C_4H_9, t-C_4H_9,$   
 $trans-CH_2=CHC_6H_5,$   
 $C\equiv CC_6H_5, C_6H_5$



These alkyl- and arylindium porphyrins undergo insertion of  $\text{SO}_2$  into the In-C bond to afford alkyl(aryl)sulfinatoindium porphyrins,  $(\text{TPP})\text{InSO}_2\text{R}$  and  $(\text{OEP})\text{InSO}_2\text{R}$  ( $\text{R} = \text{CH}_3$ ,  $t\text{-C}_4\text{H}_9$ ,  $\text{C}_6\text{H}_5$ ). Moreover, the sulfinatoindium complexes are oxidized spontaneously in refluxing anhydrous toluene as oxygen is bubbled through to give the sulfonatoindium complexes,  $(\text{TPP})\text{InSO}_3\text{R}$  and  $(\text{OEP})\text{InSO}_3\text{R}$ . A mixture of the sulfinato- and sulfonatoindium complexes was obtained also by photochemical oxidation of thioalkyl- or thioarylindium porphyrins,  $(\text{Por})\text{InSR}$ , in anhydrous toluene at room temperature. However, only the sulfinatoindium complex was isolated at  $0^\circ\text{C}$  and only the sulfonatoindium complex was formed at  $50^\circ\text{C}$ . Of these complexes,  $(\text{TPP})\text{InSO}_3\text{CH}_3$  was studied by X-ray diffraction, which has revealed that the crystal structure consists of infinite polymeric chains, as shown in Fig. 3. The In atoms lie on the inversion centers and are rigorously inside the plane defined by four N atoms [28].

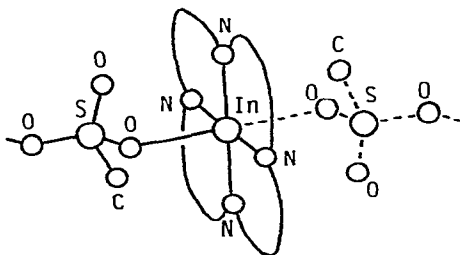


Fig. 3. Structure around the In atom of  $(\text{TPP})\text{InSO}_3\text{CH}_3$ .

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